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# Characterization and photocatalytic performance of carbon nanotube material-modified $TiO_2$ synthesized by using the hot CVD process

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ABSTRACT

Carbon nanotube-modified $TiO_2$ was synthesized by using the hot CVD process. Fe (0.13–1.9 wt%) as the catalyst for synthesis of carbon nanotubes modified on the surface of $TiO_2$, was loaded on commercial $TiO_2$ particles. $CH_4$ gas was used as the carbon source in the CVD process. The color of the Fe-supported $TiO_2$ powder changed to black when CVD treatment was performed. Nano-sized spherical carbon materials were generated on the surface of $TiO_2$ after the CVD process. The spherical materials gradually changed to carbon nanotubes with increase in CVD treatment temperature. When the CVD process was performed under optimized conditions, the photocatalytic activity of the carbon nanotube-modified $TiO_2$ was drastically increased. These results indicated that photoexcited electrons might pass through the carbon nanotubes on the surface of $TiO_2$ resulting in improvement in charge separation between electrons and holes generated photocatalytically. For our system, the carbon nanotube materials were grown directly on the surface of $TiO_2$ and this might induce strong interaction between carbon nanotubes and $TiO_2$. Meanwhile, the long-range $\pi$ electronic conjugation of nanotubes is of benefit to accelerate electron transfer. Thus, the photogenerated electrons of $TiO_2$ are rapidly transported to the carbon nanotube materials bound to the surface of $TiO_2$. The transfer of electrons generated in $TiO_2$ to carbon nanotubes was confirmed by photodeposition of Pt particles by reduction of $Pt^{4+}$ ions.



## 1. Introduction

Semiconductor particles are attractive materials as a photocatalyst because of the large number of surface reaction sites, and semiconductor particles with a large surface area have been utilized for various photocatalytic reactions, such as organic decomposition and water splitting [1–4]. Photocatalytic reaction over semiconductor particles is caused by excited electrons and positive holes, which migrate in the bulk and induce reduction and oxidation, respectively, by reacting with adsorbed species on the surface. However, both of these reactions proceed in neighboring sites on the same particle, and back reaction (including recombination) easily occurs, resulting in decline of photocatalytic efficiency. The back reaction is more likely to occur in the case of small particles because electrons and positive holes cannot be sufficiently separated from each other in the limited spatial region. Therefore, reduction of crystal size sometimes decreases photocatalytic activity due to increase in back reaction as well as decrease in crystallinity, which is correlated with recombination rate and is also a determinant factor of photocatalytic activity. Therefore, if the electrons excited by photoirradiation are separated from the holes, the photocatalytic performance of $TiO_2$ will be improved.

Ou et al. investigated the hydrogen evolution from water on MWNT-$TiO_2$:Ni composite catalysts in the presence of methanol as a sacrificial reagent under visible light [5]. Zein et al. reported preparation of Mn/Ni/$TiO_2$ catalysts that were used the for the production of hydrogen and carbon nanotubes from methane decomposition [6]. de los Arcos et al. developed Fe ions as catalysts for preparation of CNTs using $Al_2O_3$, TiN, or $TiO_2$ as a substrate [7].

In this study, we synthesized a hybrid material of $TiO_2$ particles and carbon nanotubes by using the hot filament CVD method, and we investigated the effect of carbon nanotubes introduced on the surface of $TiO_2$ photocatalysts for decomposition of acetaldehyde in gas phase under aerated conditions.

## 2. Experimental

### 2.1. Materials and instruments

$TiO_2$ (MT-600B) particles having a rutile phase were obtained from TAYCA. The specific surface area of MT-600B was 27 $m^2\,g^{-1}$. $Fe(NO_3)_2\cdot 9H_2O$ was obtained from Wako Chemical Co. Ltd. Acetaldehyde ($CH_3CHO$) was obtained from Aldrich, and other

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chemicals were obtained from commercial sources as guaranteed reagents and were used without further purification. The crystal structures of $TiO_2$ particles were determined from X-ray diffraction patterns measured with an X-ray diffractometer (JEOL, JDX3500) with a Cu target K$\alpha$-ray ($\lambda$ = 1.5405 Å). The specific surface areas of the particles were determined by using a surface area analyzer (Micromeritics, FlowSorb II 2300). The diffuse reflection (DR) spectra were measured using a Shimadzu UV-2500PC spectrophotometer equipped with an integrating sphere unit (ISR-240A). X-ray photoelectron spectra (XPS) of the $TiO_2$ particles were measured using a JEOL JPS90SX photoelectron spectrometer with an Mg K$\alpha$ source (1253.6 eV). The shift of binding energy due to relative surface charging was corrected using the C 1s level at 284.6 eV as an internal standard. The morphology of prepared $TiO_2$ particles was observed by using a transmission electron microscope (TEM; Hitachi, H-9000NAR) and a scanning electron microscope (SEM; JEOL, JSM-6701FONO). ICP analysis was performed by using ICPS-8000 (Shimadzu Co. Ltd.).

The PL measurements were carried out by using a Hitachi F-2500 luminescence spectrophotometer excited by 320 nm light at room temperature. $TiO_2$ particles modified with carbon nanotube materials and non-modified $TiO_2$ particles were was used in PL measurements.

### 2.2. Preparation of carbon nanotube-modified $TiO_2$

In this study, MT-600 (average diameter: 50 nm) was used as the starting material. $Fe(NO_3)_2{\cdot}9H_2O$ was used as the Fe source for preparation of carbon nanotubes. $TiO_2$ powder (5 g) and $Fe(NO_3)_2{\cdot}9H_2O$ were suspended in ion-exchanged water (500 ml). The amount of Fe supported on $TiO_2$ was controlled by the amount of dissolved $Fe(NO_3)_2{\cdot}9H_2O$ in an aqueous medium. The suspension was stirred for more than 3 h at room temperature. After stirring, suction filtration was performed for separation of the powder. The powder was washed with ion-exchanged water until pH of the filtrate became 7 in order to remove $NO_3^-$ ions adsorbed on the surfaces of $TiO_2$ particles. After this washing process, the powder was dried under reduced pressure for 6 h at 60 °C.

The Fe-supported $TiO_2$ (0.5 g) powder was set in a hot CVD apparatus. The sample temperature was increased to reaction temperature (300, 400, 500, 600, 700 or 800 °C) in inert gas flow ($N_2$ or Ar). When the sample temperature had reached the reaction temperature, the flow of inert gas was stopped and flow of $CH_4$ at 30 SCCM was started. After the reaction process, the flow of $CH_4$ was stopped and flow of inert gas was started again, and then the sample temperature was decreased to room temperature.

SEM, TEM, XPS, BET UV–vis, XRD, and ICP were used for characterization of samples in this study.

### 2.3. Photocatalytic decomposition of acetaldehyde

Photocatalytic activity of $TiO_2$ samples was evaluated by photocatalytic decomposition of acetaldehyde. One hundred mg of $TiO_2$ particles was spread on a glass dish, and the glass dish was placed in a Tedlar bag (As One Co. Ltd.) with a volume of 125 $cm^3$. Five hundred ppm of gaseous acetaldehyde was injected into the Tedlar bag, and photoirradiation was carried out at room temperature after acetaldehyde had reached an adsorption equilibrium. The gaseous composition in the Tedlar bag was 79% of $N_2$, 21% of $O_2$, <0.1 ppm of $CO_2$ and 500 ppm of acetaldehyde, and relative humidity was *ca.* 30%. A 500-W xenon lamp (Ushio, SX-UI501XQ) was used as a light source and the wavelength of photoirradiation was controlled by a UV-35 filter (Asahi Techno Glass). Intensity of the light was adjusted to 12 mW $cm^{-2}$. Concentrations of acetaldehyde and carbon dioxide ($CO_2$) were estimated by gas chromatography (Shimadzu, GC-8A, FID detector) with an PEG-20 M 20% Celite 545 packed glass column and by gas chromatography (Shimadzu, GC-9A, FID detector) with a TCP 20% Uniport R packed column and methanizer (GL Sciences, MT-221), respectively. In photocatalytic evaluation, P-25 (Japan Aerosil, $S_{BET}$ = 50 $m^2$ $g^{-1}$), which is a well-known commercial $TiO_2$ photocatalyst with high photocatalytic activity, was used as a standard photocatalyst. Before the evaluation, all $TiO_2$ samples were pretreated by UV irradiation with a black light in order to remove contaminants on the $TiO_2$ surface, and all photocatalytic evaluation was carried out under the same experimental conditions, including temperature, acetaldehyde concentration, air relative humidity and incident light intensity.

### 2.4. Photodeposition of Pt and lead(IV) oxide ($PbO_2$) on $TiO_2$ particles

In order to determine reduction sites on carbon nanotube-modified $TiO_2$ particles, photodeposition of Pt was carried out [8,9]. For determination of reduction sites, an aqueous suspension of $TiO_2$ particles and an isopropyl alcohol solution (10 vol%) containing 1 mmol $dm^{-3}$ of hexachloroplatinic acid ($H_2PtCl_6{\cdot}6H_2O$) was photoirradiated with a mercury lamp (5 mW $cm^{-2}$) under an argon atmosphere with vigorous magnetic stirring. After irradiation, photodeposited samples were obtained by washing with water several times and drying.

## 3. Results and discussion

### 3.1. Characterization

The color of $TiO_2$ particles loaded with Fe ions became yellow, and the color intensity increased with increase in the amount of Fe ions. It has been reported that loading of Fe on $TiO_2$ is a promising technique for the preparation of a photocatalyst under visible light [4].

The color of the Fe-loaded $TiO_2$ particles changed to black after the CVD process at difference reaction temperatures. Moreover, the color intensity increased with increase in the amount of Fe ions loaded on $TiO_2$. The change in color of the samples indicates that

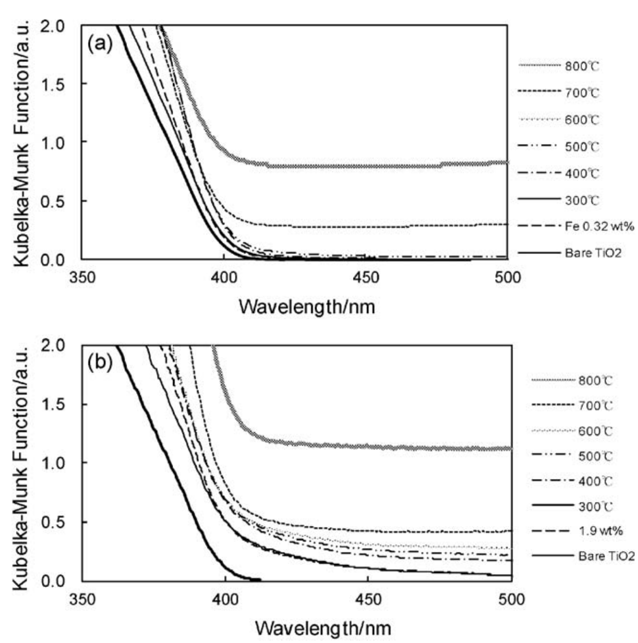


**Fig. 1.** DR spectra of carbon nanotube-modified $TiO_2$ with different amounts of Fe ions as the catalyst for generation of carbon nanotube materials and at different temperatures of CVD treatment. Amount of Fe ions: (a) 0.32 wt%; (b) 1.9 wt%.

the growth of carbon nanotubes on Fe-loaded $TiO_2$ depended on the reaction temperature.

The color of $Fe^{3+}/TiO_2$ samples was changed by modification with Fe ions and depended on the amount of Fe ions adsorbed on $TiO_2$. In addition, absorbance in the visible region drastically increased after CVD treatment. Fig. 1 shows DR spectra of bare $TiO_2$ and $Fe^{3+}/TiO_2$ samples before and after CVD treatment. The absorption edge of $Fe^{3+}/TiO_2$ samples shifted to a longer wavelength region of 400–500 nm, which corresponds to reported results [10].

For the sample after the CVD process, absorbance at wavelengths longer than 450 nm increased with increase in reaction temperature. Therefore, the CVD process should be responsible for the absorption of light at wavelengths longer than 450 nm. The DR spectra of samples shown in Fig. 1 are similar to those of MWNT-deposited $TiO_2$ reported by Ou et al. [5]. These results also indicate the growth of carbon materials including carbon nanotubes on the surface of $TiO_2$.

TEM was used to observe the microstructure of the carbon nanotube materials generated on the surface of $TiO_2$. TEM images of the samples are shown in Fig. 2. The shape of carbon materials generated on $TiO_2$ gradually changed with increase in reaction temperature of CVD treatment. In the sample after CVD treatment at 600 °C, a spherical shape of carbon materials was observed on the surface of $TiO_2$, which might be first stage of growth of carbon nanotubes. The shape of carbon materials gradually changed from a spherical shape to a tubular structure with increase in reaction temperature of CVD. Carbon nanotube materials with diameters of *ca.* 11 nm were observed on the surface of $TiO_2$ at the CVD reaction temperature of 700 °C. The amount of carbon nanotubes on the surface of $TiO_2$ nanoparticles after CVD treatment at 800 °C increased with increase in the amount of Fe ions loaded on $TiO_2$.

From these TEM images of the samples, it was confirmed that the amount of carbon nanotube materials generated on $TiO_2$ was controlled by the reaction temperature of CVD treatment and the amount of Fe ions loaded on $TiO_2$.

As mentioned previously, heat treatment is thought to be necessary during the CVD process for efficient growth of carbon nanotube materials on $TiO_2$. During heat treatment, the specific surface area of $TiO_2$ nanoparticles gradually decreased, resulting in a decrease in photocatalytic activity. Specific surface areas of the samples are shown in Fig. 3. The specific surface area did not change until the CVD treatment temperature reached 500 °C because relatively large rutile $TiO_2$ particles (particle size of *ca.*

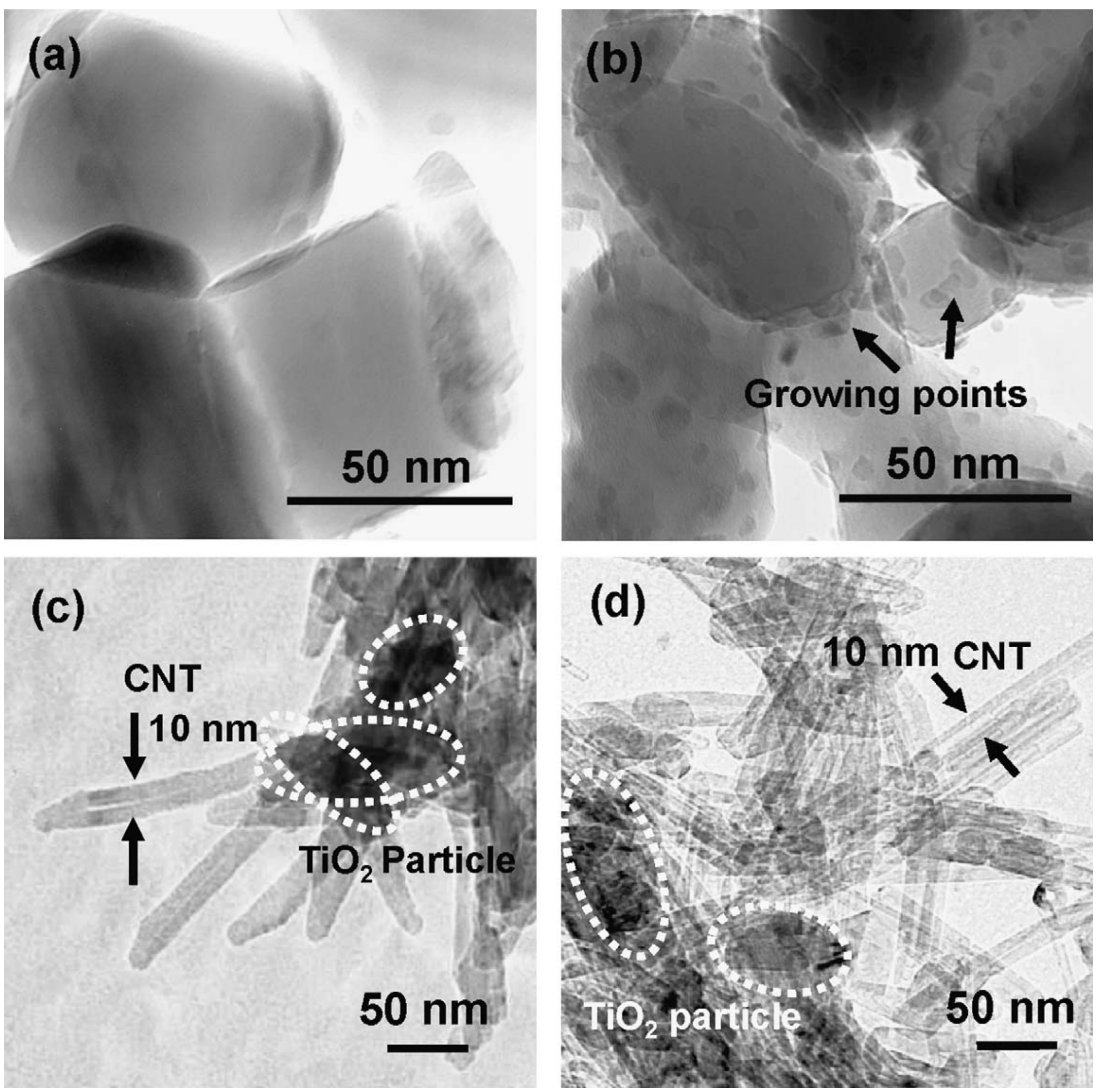


**Fig. 2.** TEM images of $TiO_2$ particles loaded with different amounts of Fe ions before and after CVD treatment at different temperatures. (a) Bare $TiO_2$ (MT-600B); (b) $TiO_2$ particles loaded with 0.32 wt% of Fe ions after CVD treatment at 600 °C; (c) $TiO_2$ particles loaded with 0.32 wt% of Fe ions after CVD treatment at 800 °C; (d) $TiO_2$ particles loaded with 1.9 wt% of Fe ions after CVD treatment at 800 °C.

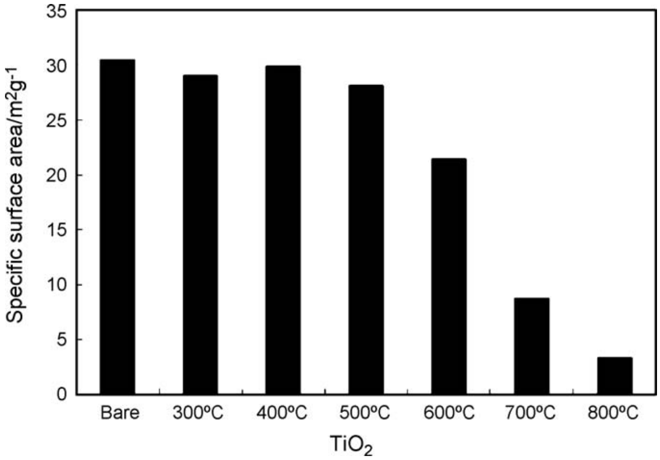


**Fig. 3.** Specific surface areas of the samples before and after CVD treatment.

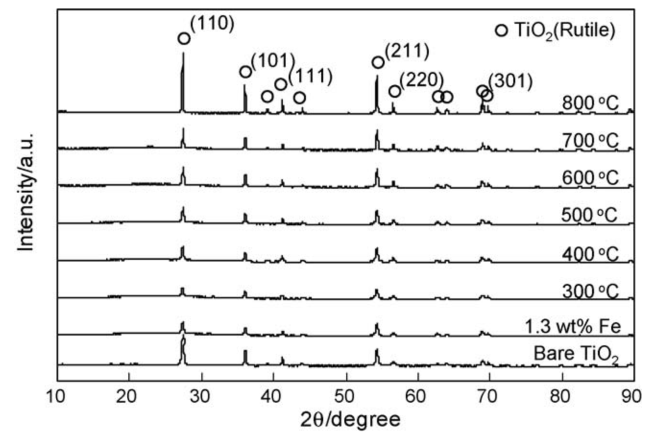


**Fig. 4.** XRD patterns of the samples before and after CVD treatment.

50 nm) might be stable at temperatures below 500 °C. At temperatures higher than 500 °C, the specific surface area drastically decrease because of sintering of rutile $TiO_2$ particles. These experimental results indicate that heat treatment below 500 °C does not affect the specific surface area of Fe-supported $TiO_2$ particles during CVD treatment.

XRD patterns of the samples are shown in Fig. 4. Peaks assigned to pure $TiO_2$ having rutile phase were observed with a wide range of CVD temperatures. There were no peaks assigned to CNT- or Fe-containing materials, such as $Fe_2O_3$ and $Fe_3O_4$, in the XRD patterns. The small amounts of these materials in the samples might be the reason for the absence of XRD peaks assigned to these materials.

XPS spectra of the samples are shown in Fig. 5. As a reference, XPS spectra of $Fe_2O_3$ are also shown. XPS peaks assigned to $Fe^{3+}$ were observed before CVD treatment. New peaks assigned to $Fe^{2+}$ appeared after CVD treatment because the CVD treatment proceeded under an inert atmosphere such as $CH_4$ or Ar at a relatively high-temperature. Under this condition, $Fe^{3+}$ deposited on $TiO_2$ was easily reduced to $Fe^{2+}$. XPS analyses were also performed after photocatalytic degradation of acetaldehyde in gas phase. After the photocatalytic reaction, only peaks assigned to $Fe^{3+}$ were observed. $Fe^{2+}$ ions on $TiO_2$ might be easily oxidized to $Fe^{3+}$ ions during photocatalytic reactions.

### *3.2. Photocatalytic degradation of acetaldehyde in gas phase over carbon nanotube material-modified $TiO_2$*

Photocatalytic activities of the carbon nanotube material-modified $TiO_2$ were evaluated, and the results are shown in Fig. 6. The sample loaded with 0.32 wt% of Fe ions and then treated by CVD at 600 °C showed the highest photocatalytic performance. The photocatalytic activity of $TiO_2$ modified with an optimum amount of carbon nanotube materials was about four times higher than that of bare $TiO_2$.

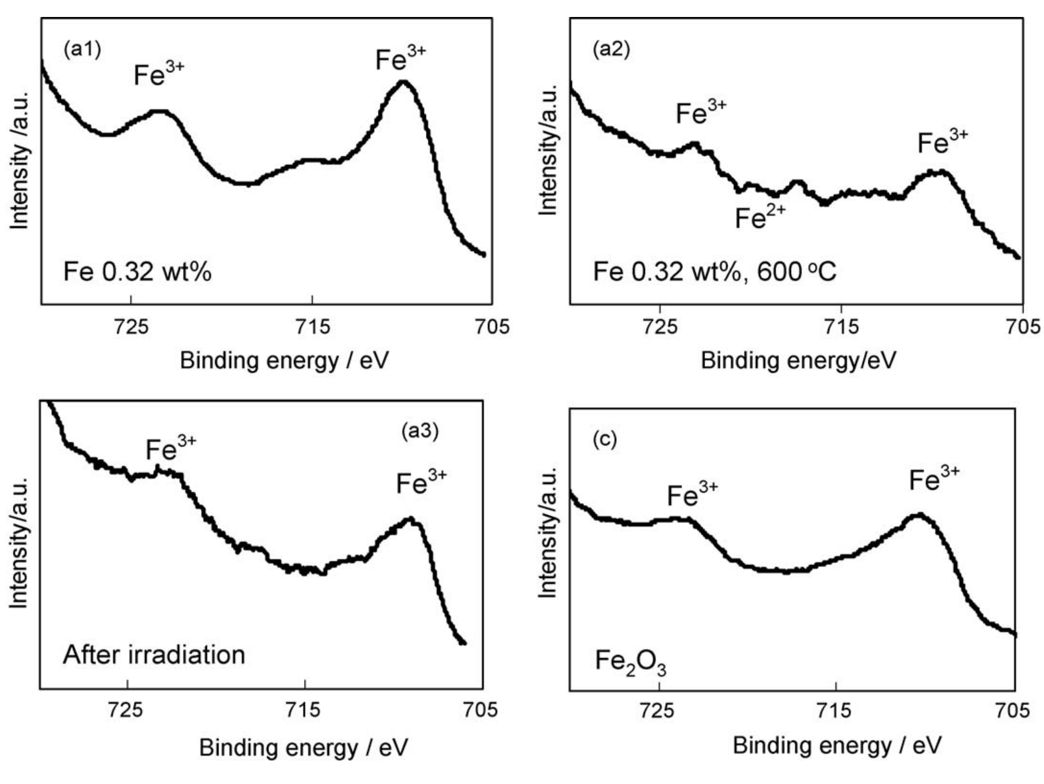


**Fig. 5.** XPS spectra of the samples. (a1) Fe(0.32 wt%)-loaded $TiO_2$ particles; (a2) after CVD treatment "a1" at 600 °C; (a3) after evaluation of photocatalytic activity for degradation of acetaldehyde in gas phase of the sample"a2"; (c) $Fe_2O_3$ as a reference.

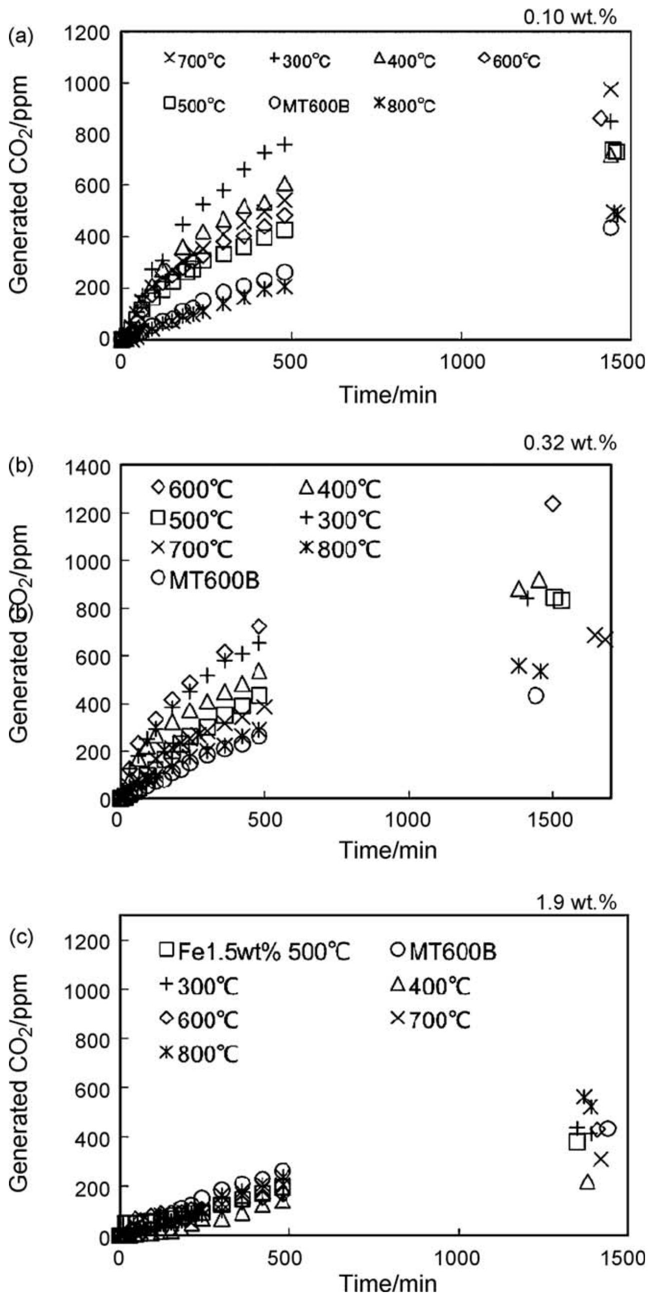


**Fig. 6.** Photocatalytic degradation of acetaldehyde in gas phase over $TiO_2$ particles modified with carbon nanotube materials and non-modified $TiO_2$ particles. Amount of Fe ions: (a) 0.10 wt%; (b) 0.32 wt%; (c) 1.90 wt%.

The photocatalytic activity of the $TiO_2$ photocatalyst modified with a larger amount of carbon nanotube material (amount of Fe ions: 1.9 wt%) drastically decreased because carbon nanotube materials on $TiO_2$ prevent incident light from penetrating $TiO_2$. On the other hand, improvement in photocatalytic activity of $TiO_2$ modified with a small amount of carbon nanotube materials (amount of Fe ions: 0.1 wt%) was less than that of photocatalytic activity of $TiO_2$ modified with an optimum amount of carbon nanotube materials (amount of Fe ions: 0.32 wt%), which is due to a decrease in charge separation between electrons and holes generated in $TiO_2$ during photocatalytic reactions.

From the experimental results (characterization of samples and photocatalytic performance), we can summarize the relationships between CVD treatment temperature, amount of Fe ions loaded on the surface of $TiO_2$, and photocatalytic activity for degradation of acetaldehyde.

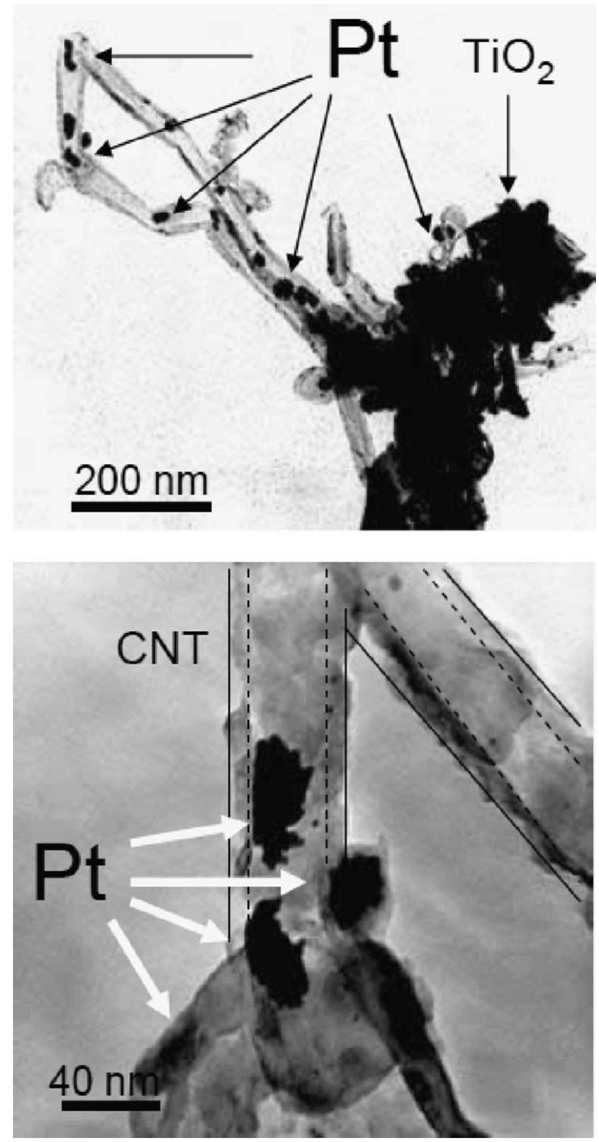


**Fig. 7.** TEM images of the carbon nanotube materials-modified $TiO_2$ after photodeposition of Pt particles.

*3.2.1. In the case of low-temperature CVD treatment*

The amount of carbon nanotube materials generated on $TiO_2$ is small because the amount of dissolved $CH_4$, which is the carbon source in the CVD process, is small. When the amount of carbon

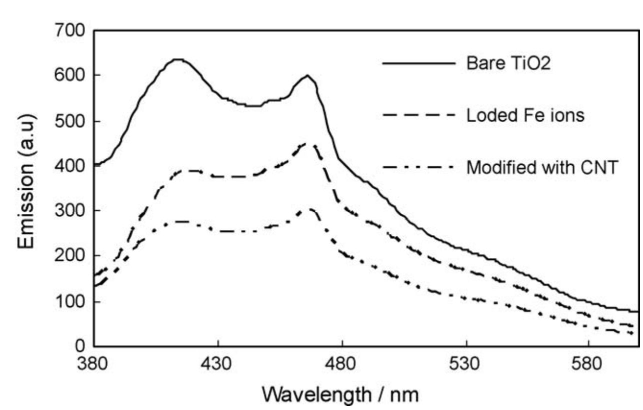


**Fig. 8.** Photoluminescence (PL) spectra: comparison of samples of bare $TiO_2$ and $TiO_2$ modified with carbon nanotube materials.

nanotube materials on $TiO_2$ is small, recombination of electrons and holes, which are generated by photoirradiation, should not be suppressed. As a result, the carbon nanotube material-modified $TiO_2$ would have low performance.

*3.2.2. In the case of high-temperature CVD treatment*

When the reaction temperature of the CVD process was higher than 500 °C, $TiO_2$ particles, which are the starting material in this study, should sinter, resulting in a small specific surface area of the photocatalyst. At the same time, a large amount of carbon nanotube materials covered the surface of $TiO_2$. The small surface area of the photocatalyst would cause low performance because the number of active sites is decreased. The amount of carbon nanotube materials generated should be large when the CVD process is performed at a high-temperature. The excessive amount of CNT should prevent incident light from penetrating the surface of $TiO_2$. Therefore, the photocatalytic performance should drastically decrease.

*3.2.3. In the case of a small amount of Fe ions*

The amount of carbon nanotube materials generated by the CVD process should be small because Fe ions act as catalysts for the generation of carbon nanotube materials. When the amount of carbon nanotube materials on the $TiO_2$ surface is small, charge separation of electrons and holes would not be improved. As a result, the photocatalytic activity of carbon nanotube material-modified $TiO_2$ would be relatively low.

*3.2.4. In the case of a large amount of Fe ions*

The amount of carbon nanotube materials generated by the CVD process should be large when using a large amount of Fe ions that act as catalysts for the generation of carbon nanotube materials. The intensity of incident light that reached the surface of $TiO_2$ by passing through the carbon nanotube materials attached to the surface of $TiO_2$ decreased in the presence of an excessive amount of carbon nanotube materials on $TiO_2$ particles. Therefore, the photocatalytic performance of the carbon nanotube material-modified $TiO_2$ should be low.

### 3.3. Photodeposition of Pt for determination of reduction sites

The carbon nanotube materials introduced on the surface of $TiO_2$ are thought to play a role for picking up photoexcited electrons generated in $TiO_2$, resulting in improvement in charge separation between electrons and holes because the electrons can move freely through the walls of nanotubes [11].

In order to investigate the effect of carbon nanotube materials attached to the surface of $TiO_2$, photodeposition of Pt was performed. TEM images of the sample after the photo electrodeposition process are shown in this figure, as shown in Fig. 7, Pt particles, which were identified by EDX analysis, were deposited inside the carbon nanotube. Pt particles of a few nanometers in size were only observed inside the carbon nanotube materials, and there was no deposition of Pt particles on $TiO_2$, which was also confirmed by EDX analyses. In the photodeposition process, $Pt^{4+}$ ions are reduced by the photoexcited electrons generated in $TiO_2$ particles [8,9]. The electrons generated in $TiO_2$ particles should transfer to the carbon nanotubes attached on $TiO_2$ and react with $Pt^{4+}$ ions to deposit Pt particles because Pt particles were deposited inside the carbon nanotubes. Therefore, the carbon nanotubes introduced on $TiO_2$ play an important role for picking up photoexcited electrons generated in $TiO_2$, resulting in improvement of charge separation between electrons and holes.

### 3.4. PL spectra analyses of $TiO_2$ before and after modification with carbon nanotube materials

PL emission spectra have been widely used for investigating the efficiency of charge carrier trapping, migration and transfer and for investigating the fate of electron and hole pairs in semiconductor particles [12]. In order to investigate the effect of carbon nanotube materials introduced on the surface of $TiO_2$ on suppression of the recombination of electrons and holes produced by $TiO_2$, PL spectra of $TiO_2$ particles modified with carbon nanotube materials were analyzed as shown in Fig. 8. $TiO_2$ particles showed a broad PL emission band similar to the results of a previous study [13]. The emission band corresponding to the peak position of about 525 nm is for anatase $TiO_2$ powder [14]. Compared with the spectrum of $TiO_2$, it was found that the intensity of PL spectra of the carbon nanotube materials-modified $TiO_2$ particles in the same range of wavelengths was much lower than that of bare $TiO_2$. The reduction of PL intensity in the carbon nanotube materials-modified $TiO_2$ indicates a decrease in the radiative recombination process between photoexcited electrons and holes because the observed PL spectrum in $TiO_2$ can be attributed to the radiative recombination process of self-trapped excitations [12,13,15].

## 4. Conclusions

Fe ion-loaded $TiO_2$ particles were treated by the CVD process for the synthesis of $TiO_2$ particles modified with carbon nanotube materials. After the CVD process with $CH_4$ flow, the color of the sample changed from yellow to black, due to generation of carbon nanotube materials on the surface of $TiO_2$. The photocatalytic performance of the carbon nanotube materials-modified $TiO_2$ powders for degradation of acetaldehyde in gas phase was about four times higher than that of bare $TiO_2$. The carbon nanotube materials introduced on the surface of $TiO_2$ play an important role for picking up photoexcited electrons generated in $TiO_2$, resulting in improvement in charge separation electrons and holes. These results were confirmed by photodeposition of Pt particles and PL measurements.

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